Study of the structure of AMORPHOUS CARBON using Raman, photoemission and X-ray Absorption spectroscopies

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Asturias
paraíso natural

Acknowledgements

Samples preparation:

- *Simon Anders*

Beam line 9.3.2:

- *Zahid Hussain*
- *Xing Zhou*
- *Scott Kellar*
- *Eddy Moler*

Properties:

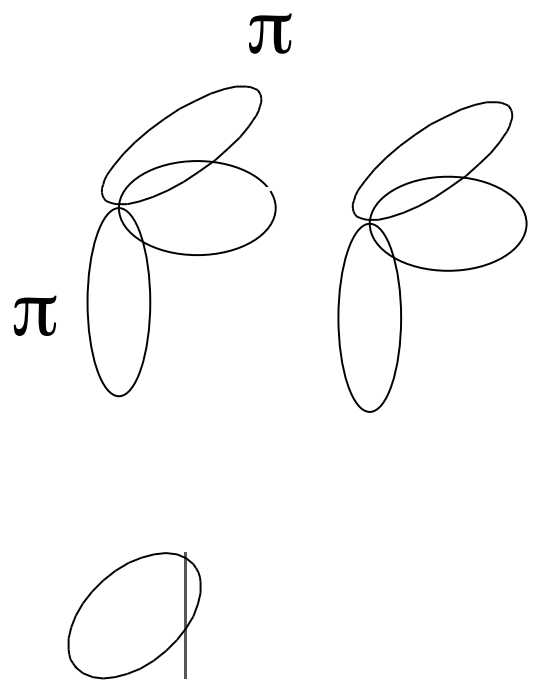
- ***Mechanical***
  - ***+Hardness:* 60-100 GPa** *(Diamond: 100 GPa.)*
  - ***+Young Modulus:* 400-500 GPa.** *(Diamond: 1000 Gpa. SiC: 450 Gpa.)*
- ***Chemically inert***
- ***Amorphous semiconductor***
  - ***Low density of dangling bonds*** *(differing from a-Si, a-Ge...)*
- ***Applications***
  - ***+Hard discs protecting layer***
  - ***+Multilayers for X-ray optics (W/C, Si/C)***
  - ***+Alternative to a-Si***
  - ***+Field emitters for flat pannel displays***

Chemical bonding in carbon:
2s & 2p orbital hybridization

sp

1D

d=1.2 A



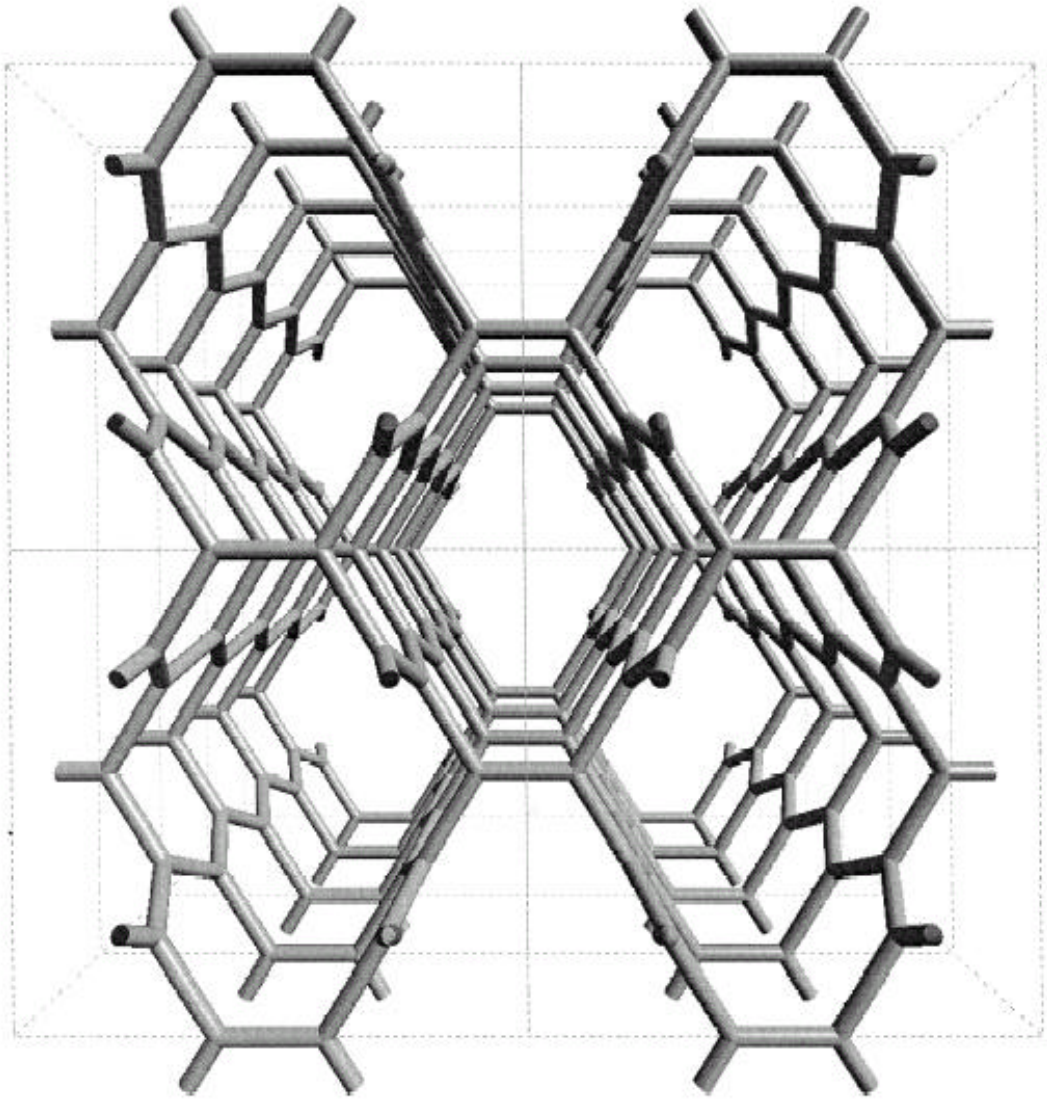
sp^3

3D

Diamond

d=1.54 A

3D "all sp^2" carbon crystal

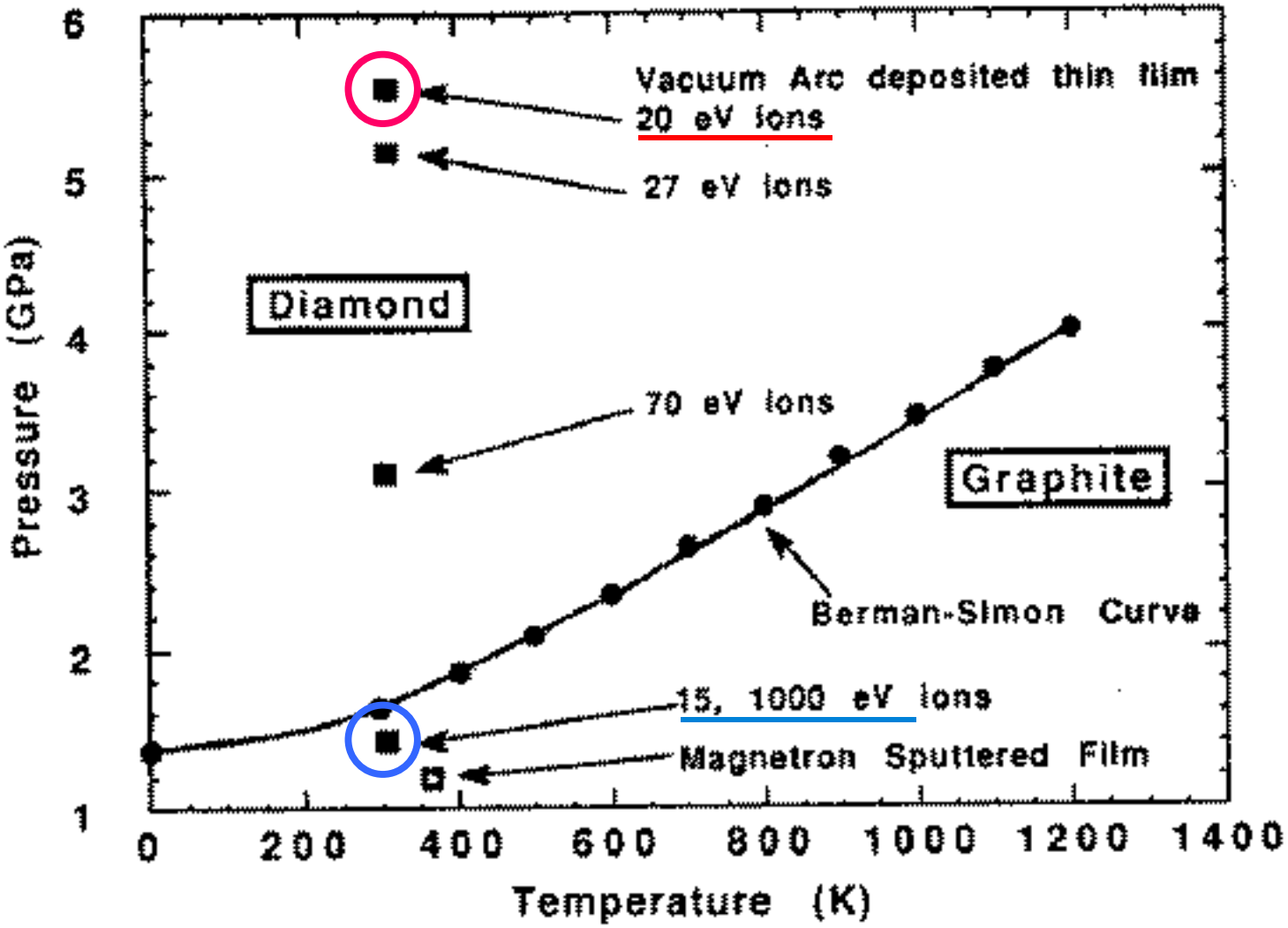


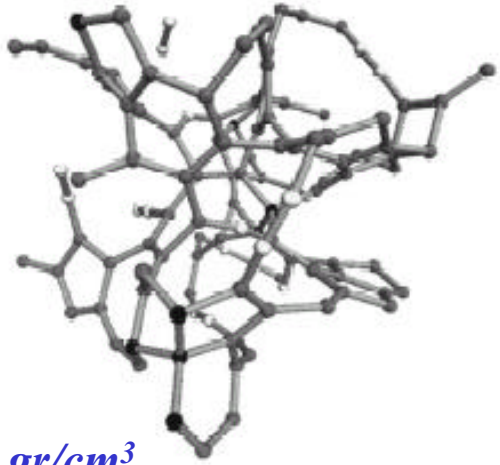
- π bonds are **less energetic** (2 eV) than σ (5 eV)
- π bonds form aromatic molecules

  +**conjugation** (*delocalization*)

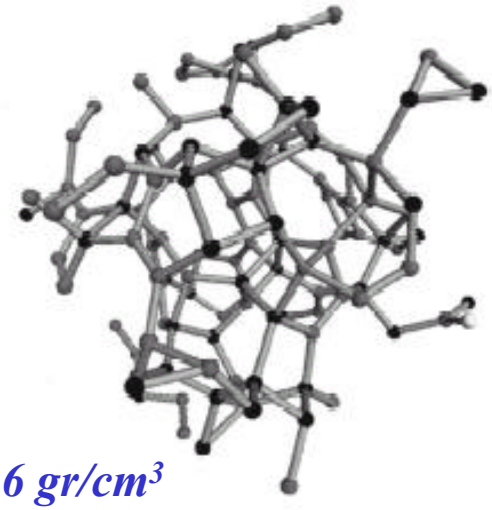
  +**Locally planar, less compact** structures

Sample preparation: Energetic process

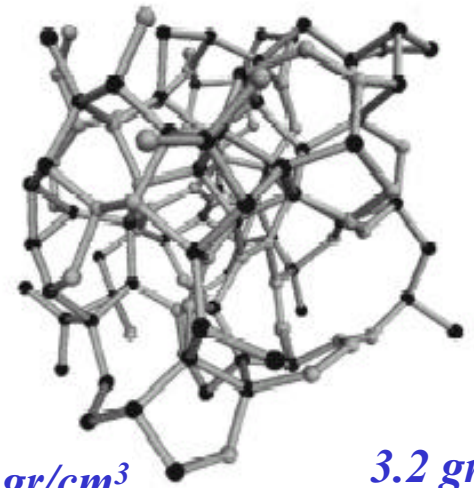




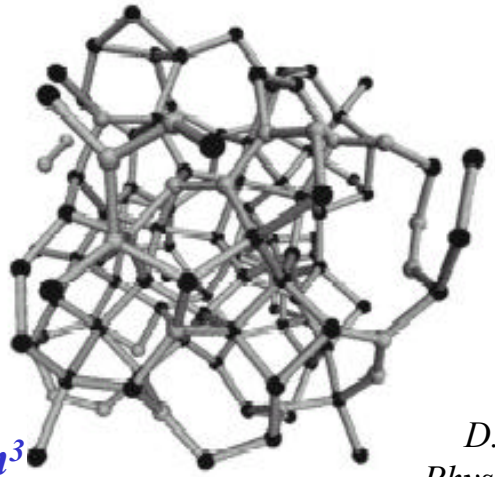
2.0 gr/cm³



2.6 gr/cm³



2.9 gr/cm³



3.2 gr/cm³

D. G. McGulloch et al.
Phys. Rev. B ***61*** *(2000) 2349*

Structural Characterizationof amorphous:

Spectroscopies sensitive to the local environment of atoms

RAMAN , PHOTOEMISSION, X-RAY ABSORPTION

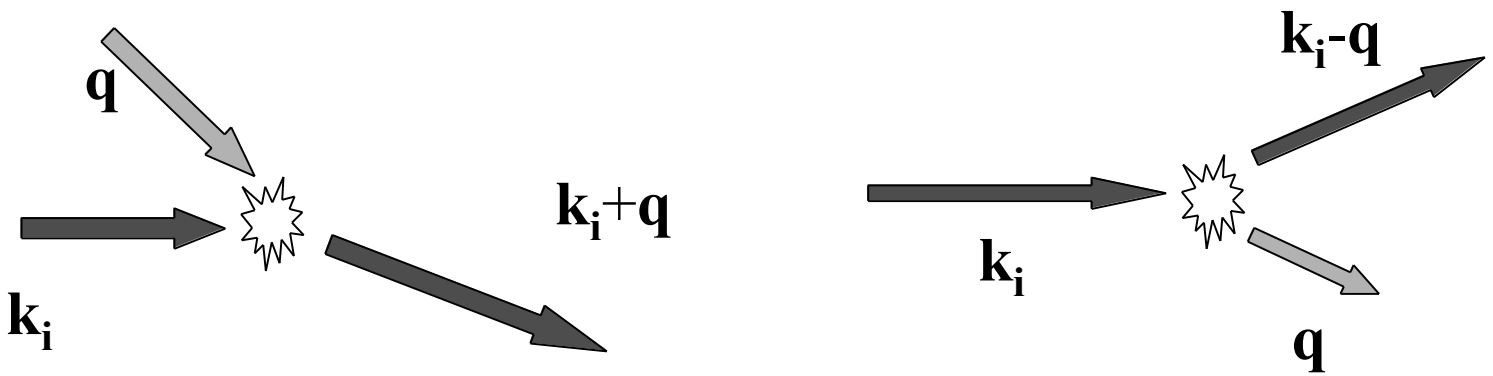
Raman Spectroscopy

$$P=\chi(\omega_i,\mathbf{k}_i)E\cos(\mathbf{k}_i\,\mathbf{r}-\omega_i t)=$$

$$\chi_0(\omega_i,\mathbf{k}_i)E\cos(\mathbf{k}_i\,\mathbf{r}-\omega_i t)+(\delta\chi_0/\delta R)R\cos(\mathbf{qr}-\omega_q t)\,E\cos(\mathbf{k}_i\,\mathbf{r}-\omega_i t)=$$

$$P_0+(\delta\chi_0/\delta R)RE\{\cos[(\mathbf{k}_i+\mathbf{q})\mathbf{r}-(\omega_i+\omega_q)t]+\cos[(\mathbf{k}_i-\mathbf{q})\mathbf{r}-(\omega_i-\omega_q)t]\}=$$

$$P_0+P_{+q}+P_{-q}$$

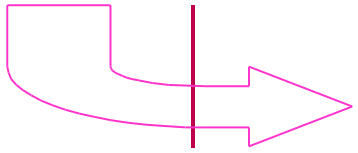


$q<2k_i$ ⟶ *Using visible light,* $q<(1/2000)A^{-1}\sim 0$

- Vibrations in a **cristal**: phonons (*plain waves*)
- In an **amorphous**: vibrations are localized

$$\Delta q \sim 1/\Delta r$$

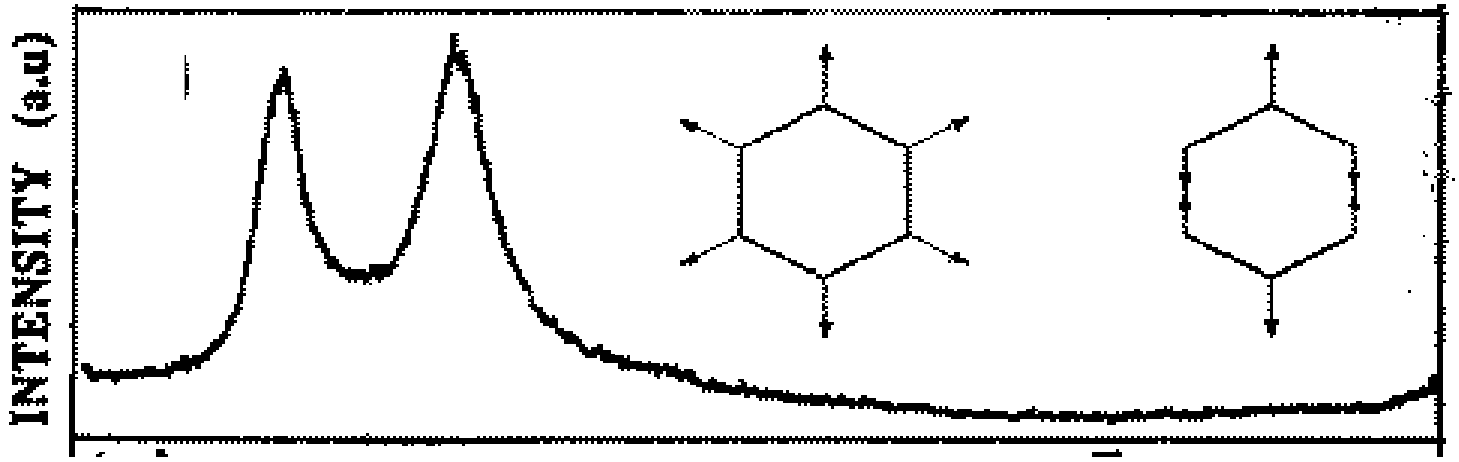
All vibration modes are excitable



Raman Spectroscopy

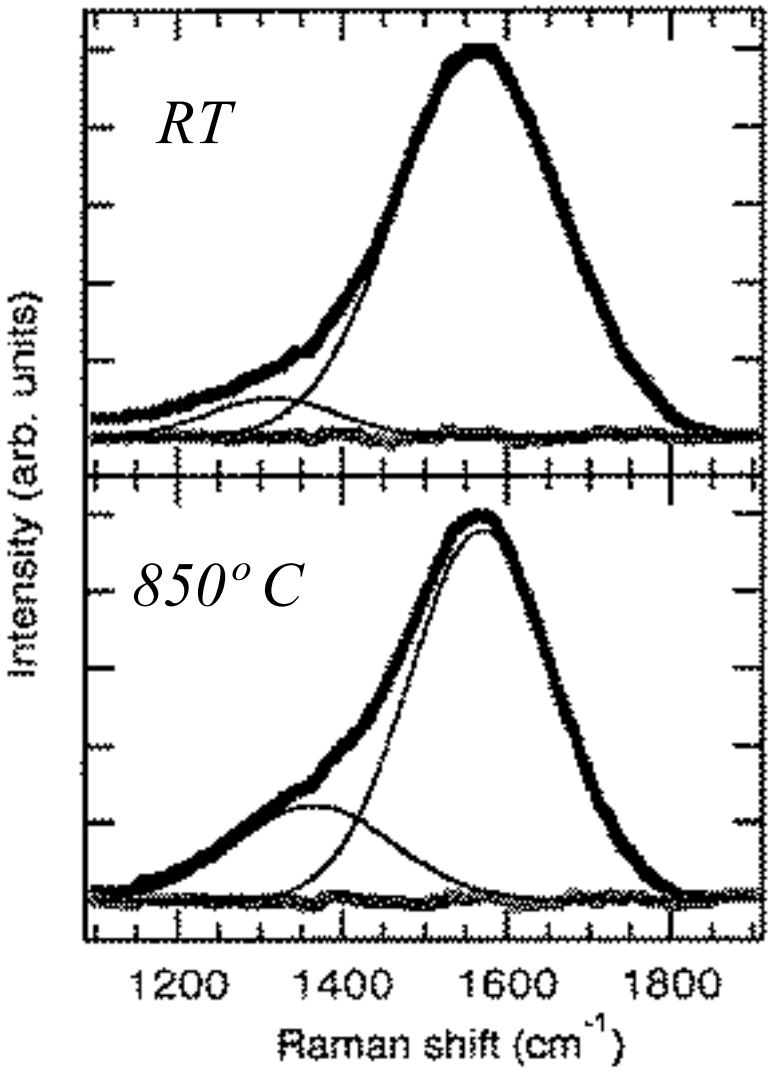
$$P_{-q} \sim (\delta \chi_0 / \delta R) R\, E$$

Sensitive to local simmetry

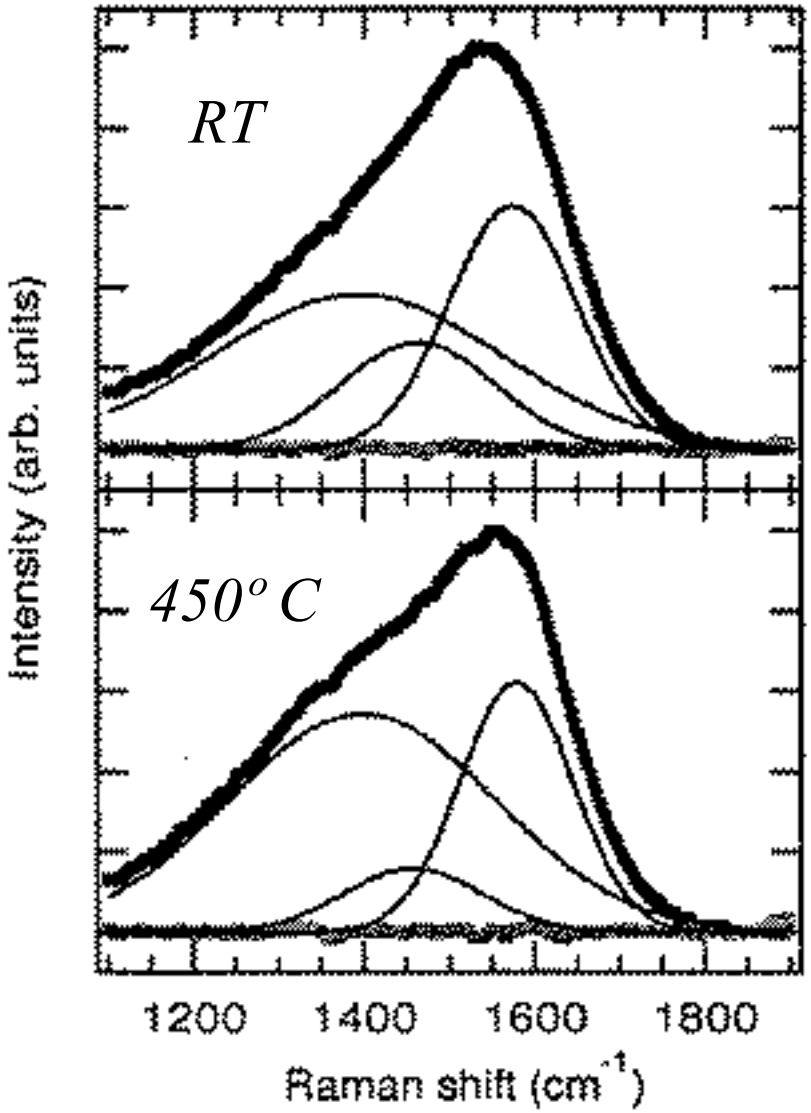


Raman Spectroscopy

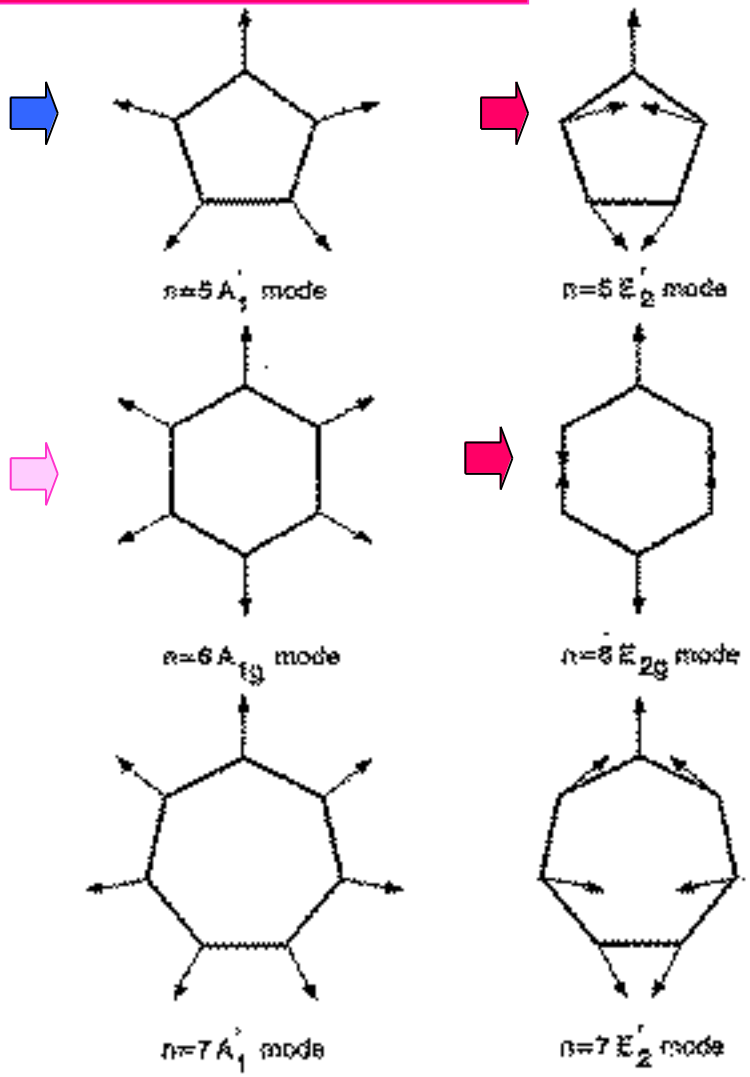
hard* a-C *(2.9 gr/cm^3)



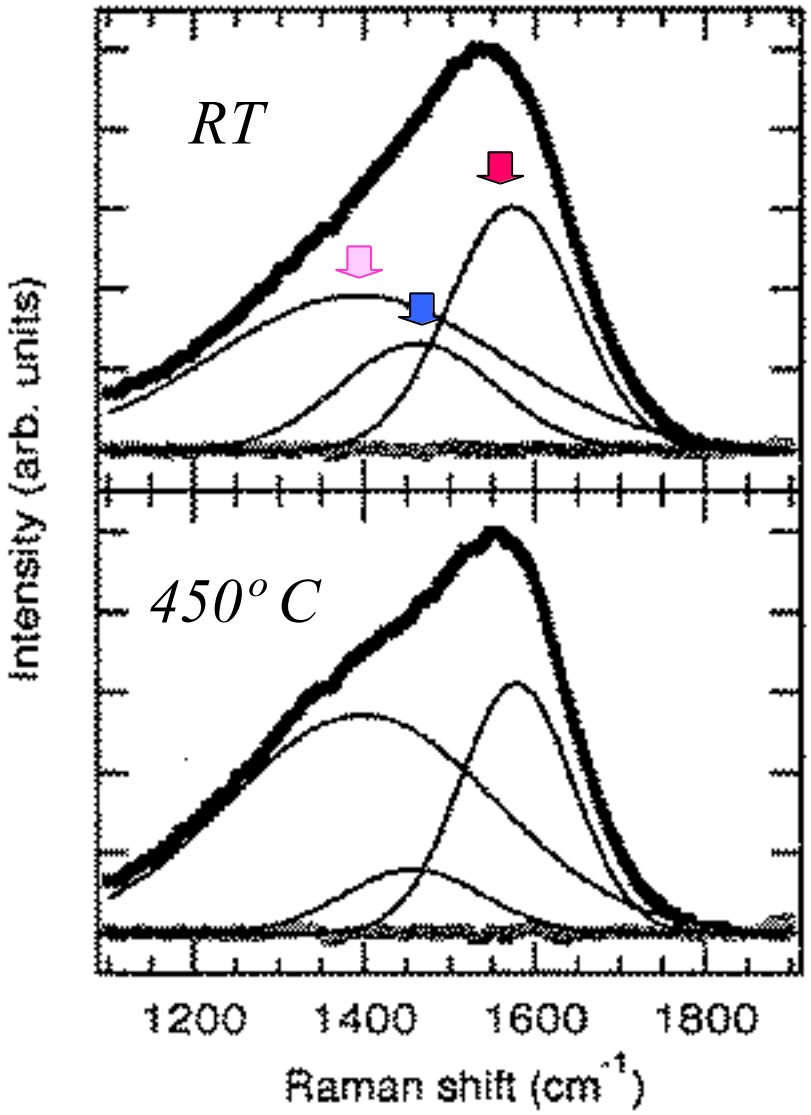
soft* a-C *(2.1 gr/ cm^3)



Raman Spectroscopy

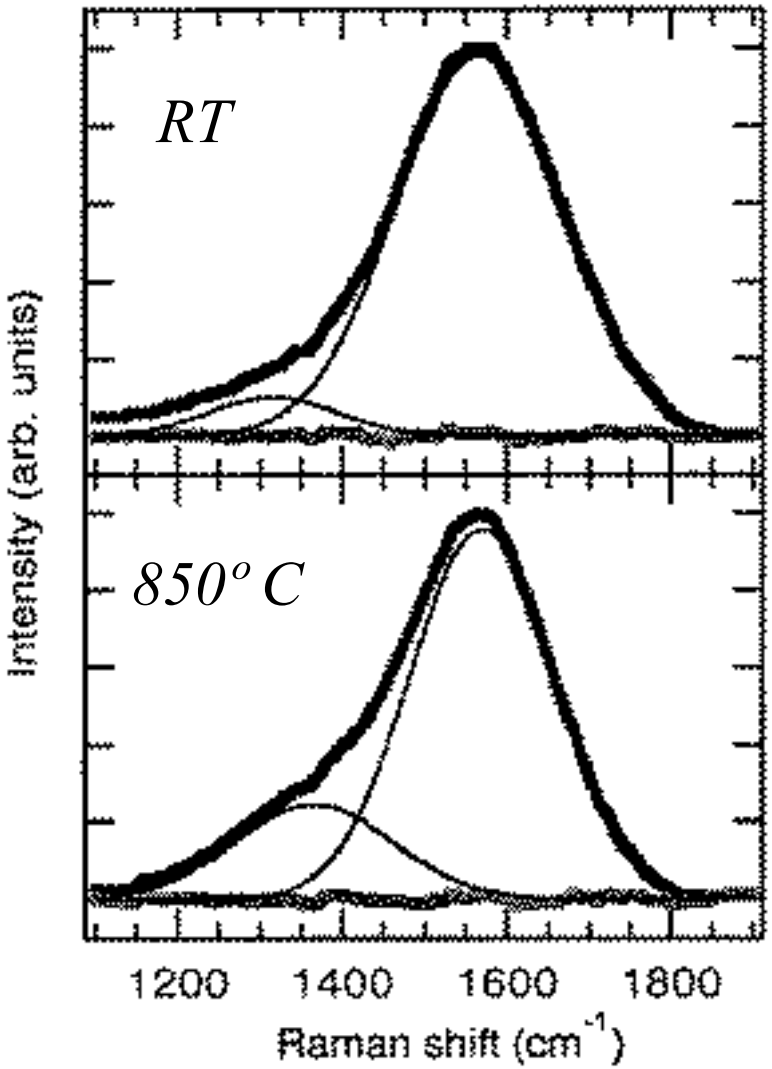


soft a-C *(2.1 gr/cm^3)*



Raman Spectroscopy

hard* a-C *(2.9 gr/cm^3)



hard a-C :

- ***Very low concentration of aromatic rings***

  → *sp^2 +sp^3 mixture?*

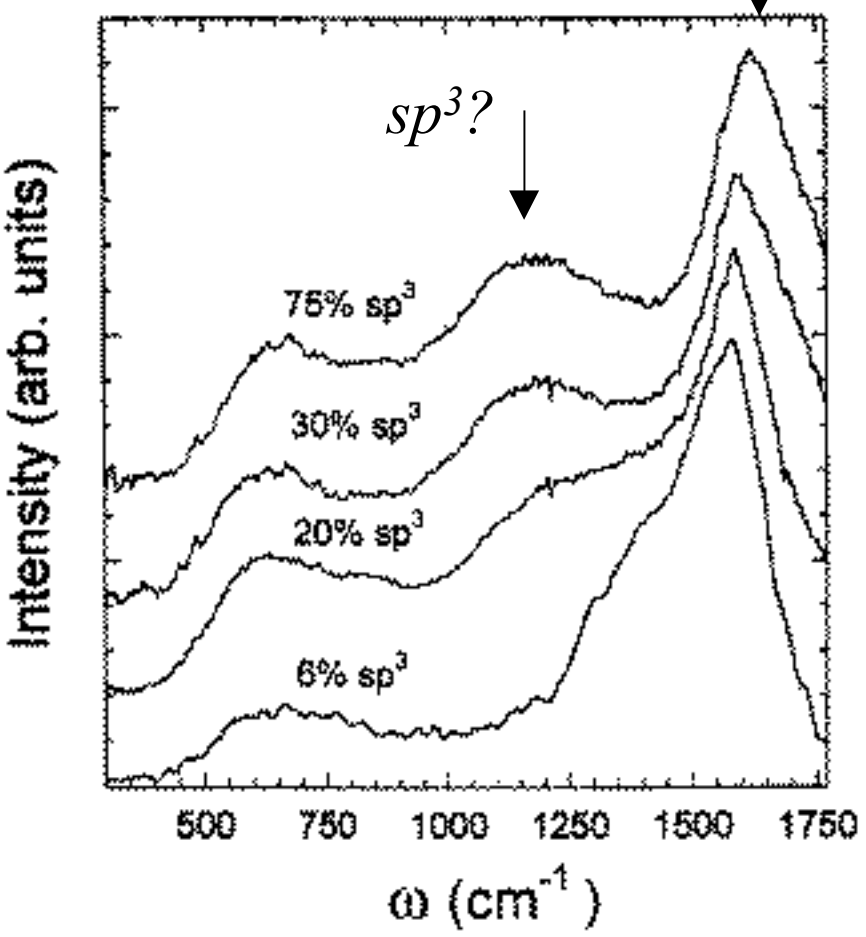
soft a-C :

- ***Aromatic rings***

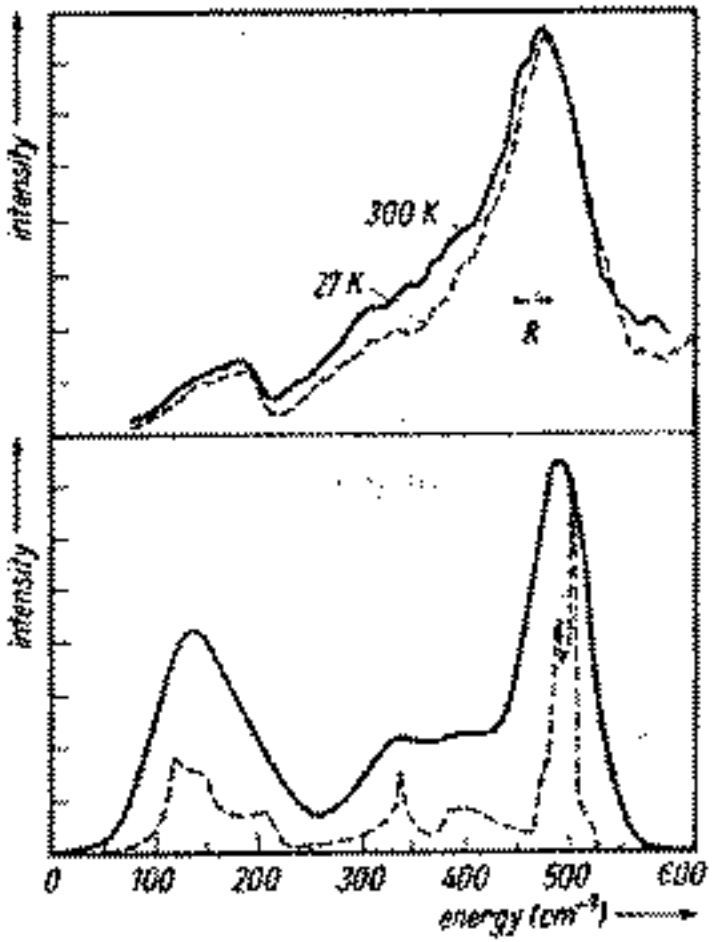
  → ***sp^3*** *to join aromatic clusters?*

Raman Spectroscopy

a-C



a-Si



Raman UV (244 nm)

Photoemission Spectroscopy (XPS-UPS)

XPS

•Core level photoemission **(C *1s*) sensitive to the environment of the excited atom**

Binding energy shifts

$$E_B = E_B^{at} + K\Delta Q + V$$

A=diamond
B=graphite

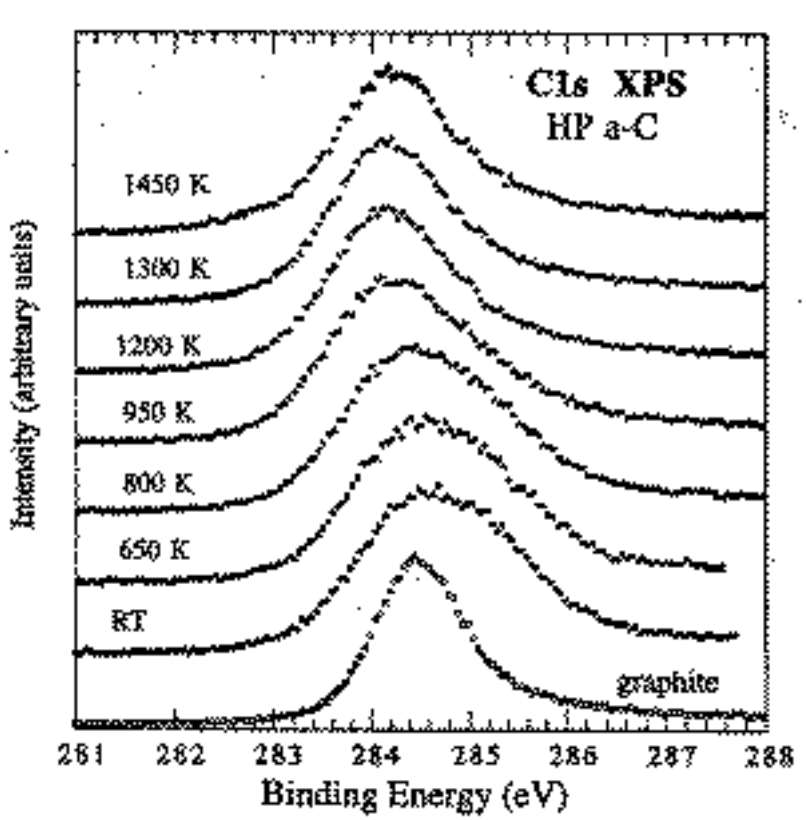
$E_B^A = 285.1$ eV
$E_B^B = 284.4$ eV

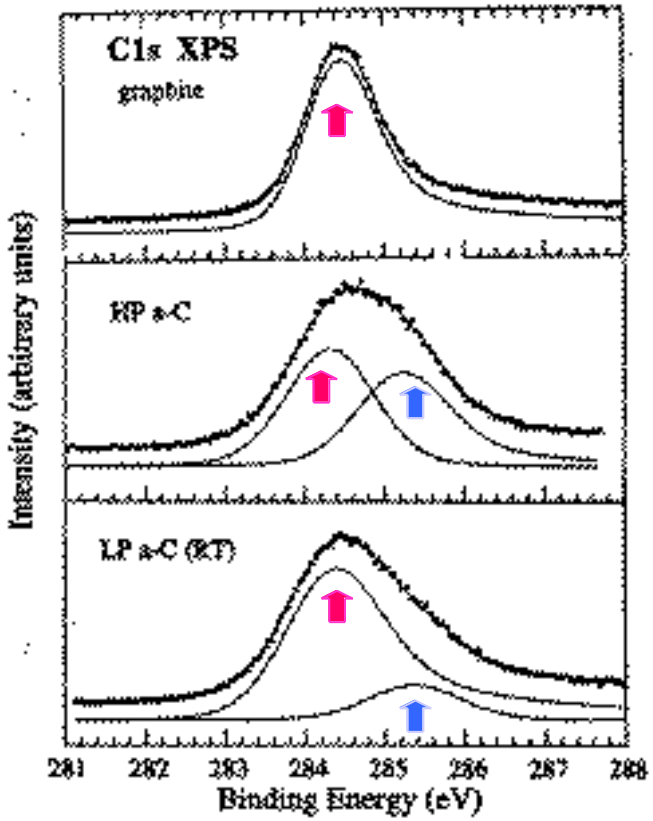
⇨ $\Delta E_B^{A-B} > 0$

• $(\Delta Q^A - \Delta Q^B) > 0$: π ***are more delocalized*** *than* σ
• $(V^A - V^B) > 0$: *more effective* ***screening*** *in graphite*

Photoemission Spectroscopy (XPS-UPS)

XPS in a-C

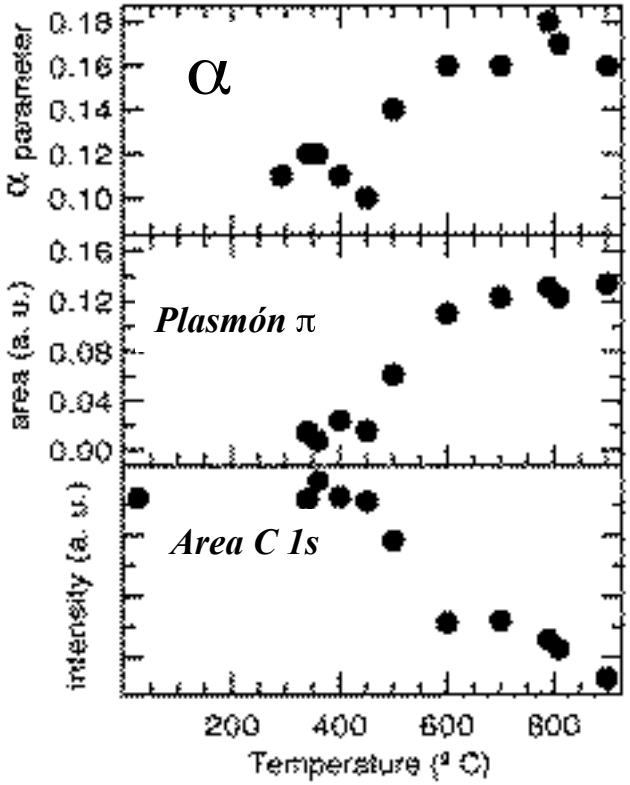


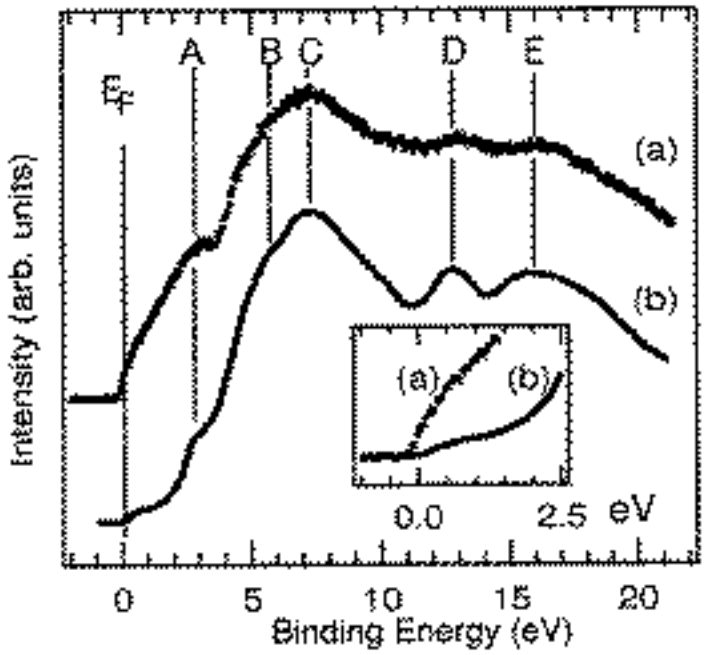


***Two different environments* with E_B simmilar to graphite and diamond**

$$I_1/I_2 = sp^2/sp^3$$

Photoemission Spectroscopy (XPS-UPS)





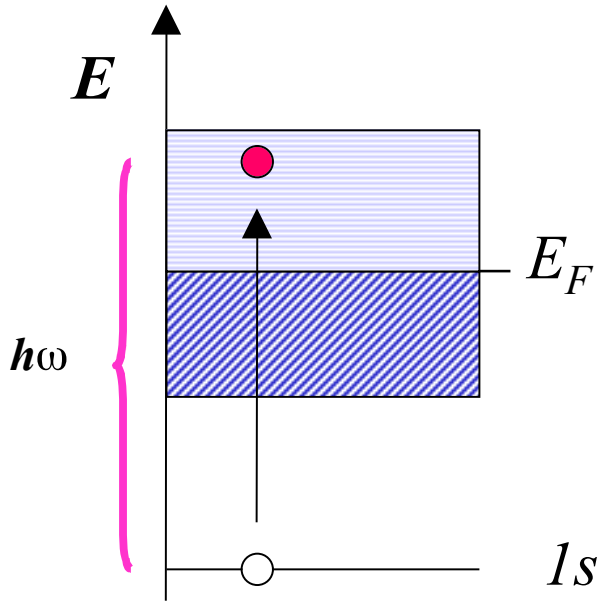
Phase Transition between 450º and 600ª C

Density of States at the E_F is higher in annealed a-C than in graphite

X-ray Absorption (NEXAFS)

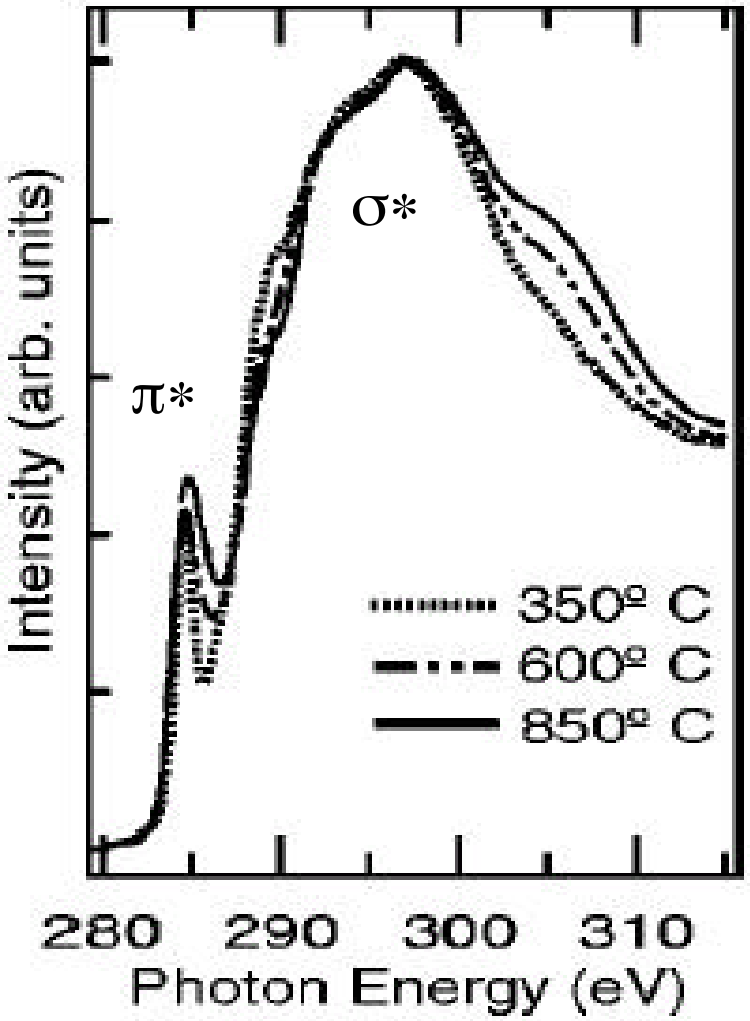
- ***NEXAFS de C 1s:***
  p-projected density of unocuppied states

$$\sigma \sim |\langle \psi_i | Ep | \psi_f \rangle|^2$$



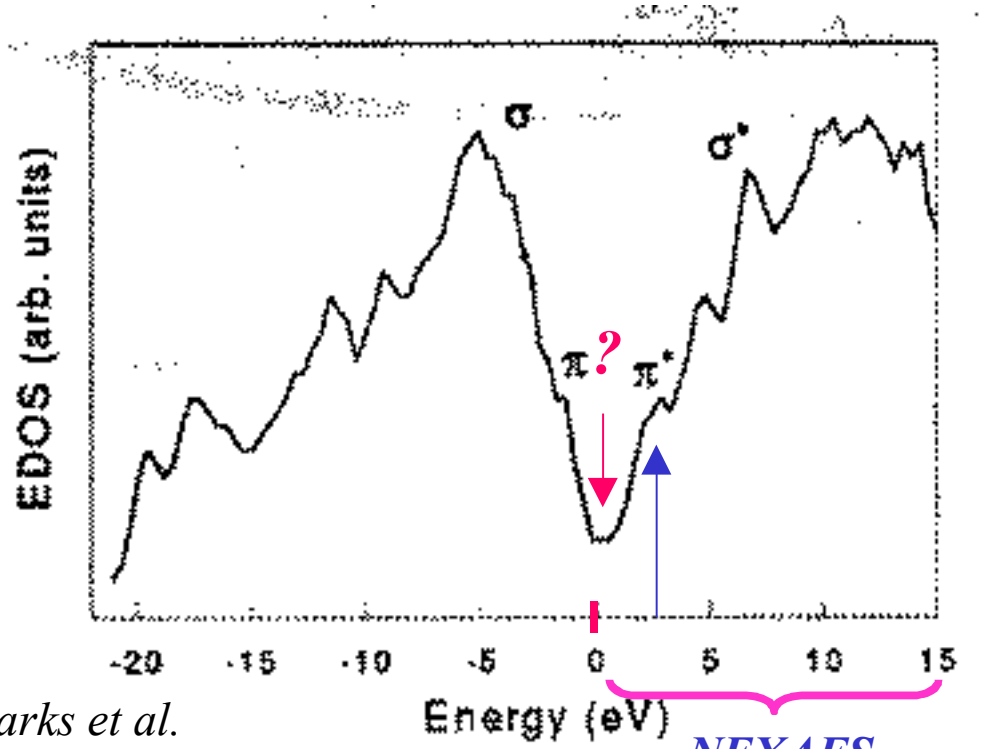
X-ray Absorption (NEXAFS)

NEXAFS:

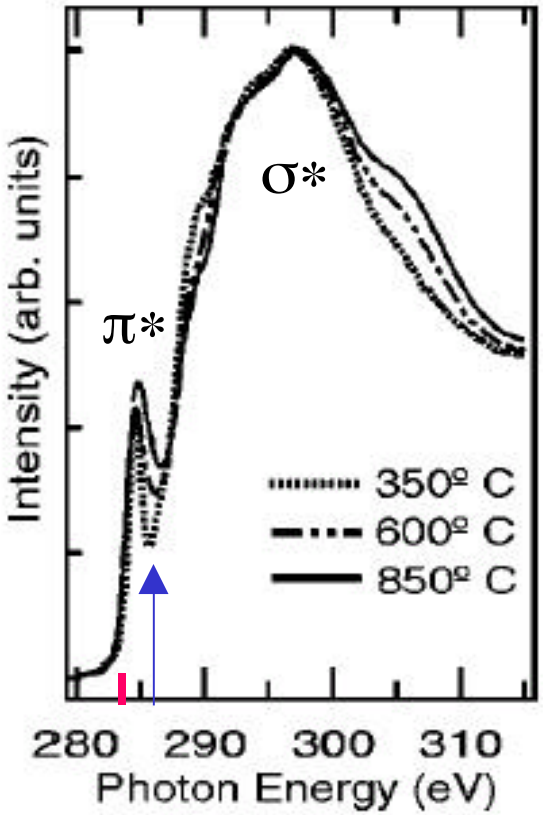


$\pi^* / \sigma^* \sim sp^2/sp^3$

X-ray Absorption (NEXAFS)



N.A. Marks et al.
PRL 76 (1996) 768



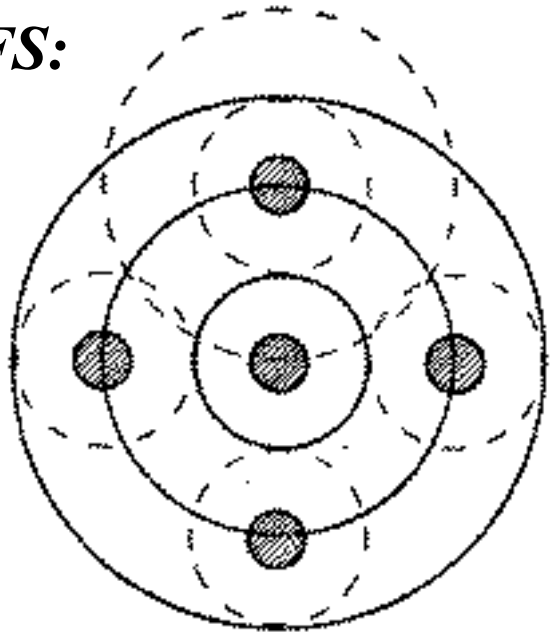
- ***What is the right intensity of π* states spectra of a-C?***

- ***What can be learn from the σ* part of the NEXAFS spectra?***

X-ray Absorption (NEXAFS)

Alternative interpretation for NEXAFS:

Scattering *of the excited* e^- *by* ***nearest neighbors***



$$\mu(E)=\mu_{at}(E)+\mu_{sol}(E)$$

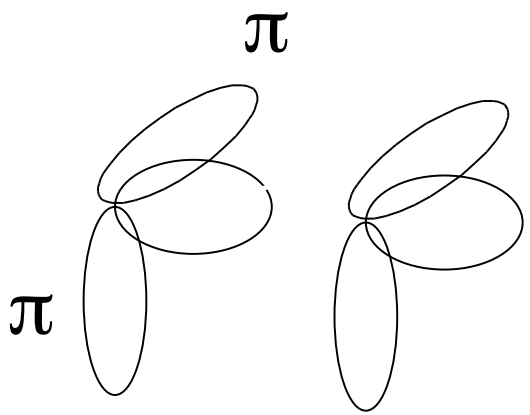
$$\mu_{sol}(k) \sim \sin(2kR+\theta)$$

$$1^{st}\ max.:\ 2kR+\theta=\pi/2$$

$$hk=\{2m(\Delta_\sigma-E_F)\}^{1/2}$$

$$\Delta_\sigma=(Ch^2/2m)R^{-2}+E_F$$

X-ray Absorption (NEXAFS)

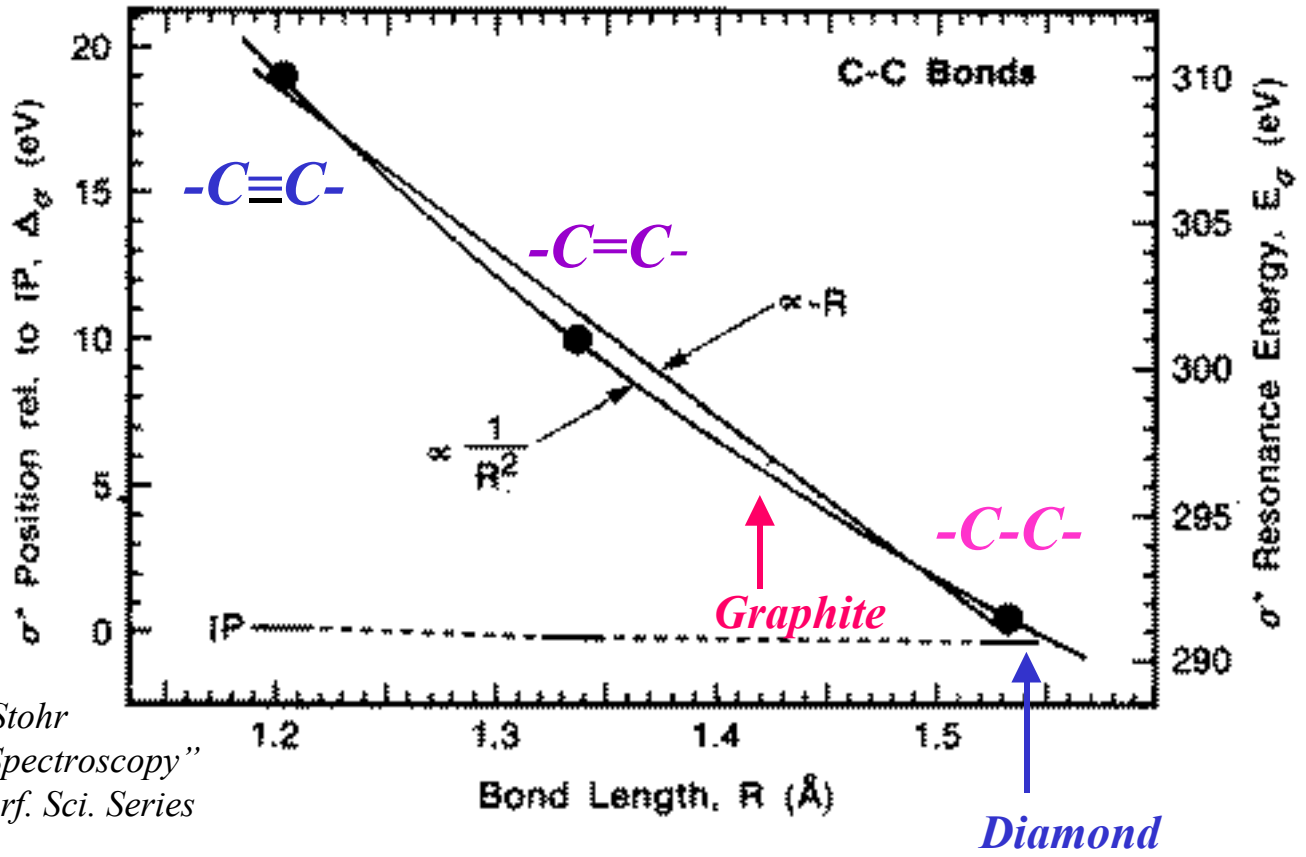


σ electrons are spatially confined,
like in an infinite potencial well

- *σ binding energy strongly dependent on R*

$$\Delta E_\sigma \sim 1/R^2$$

X-ray Absorption (NEXAFS)



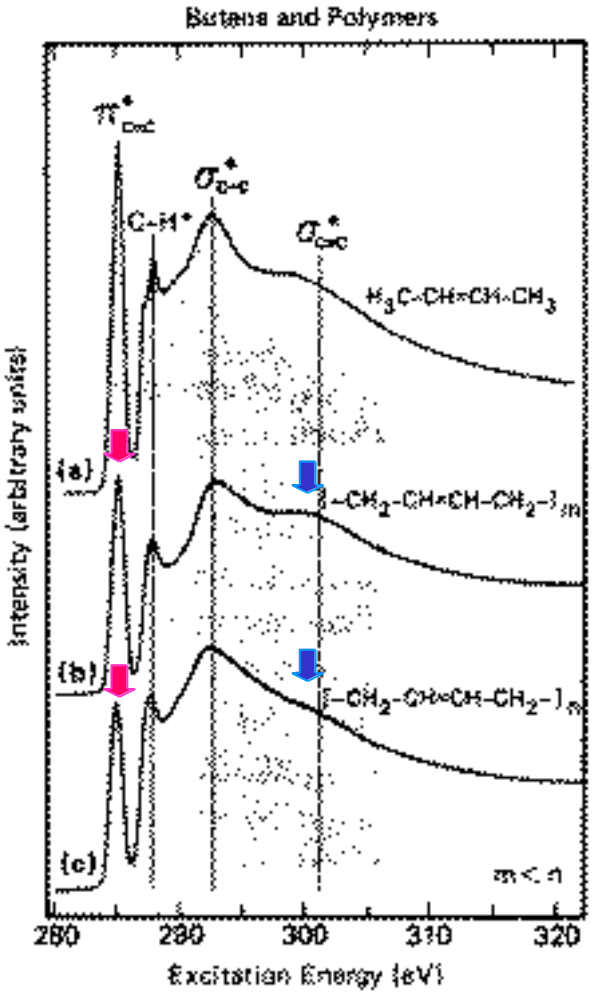
J. Stohr
"NEXAFS Spectroscopy"
Springer Surf. Sci. Series

- ***The type of bonding is determined from the σ* energy position***

X-ray Absorption (NEXAFS)

NEXAFS recognize only the atomic environment of the excited atom

"Building block" picture



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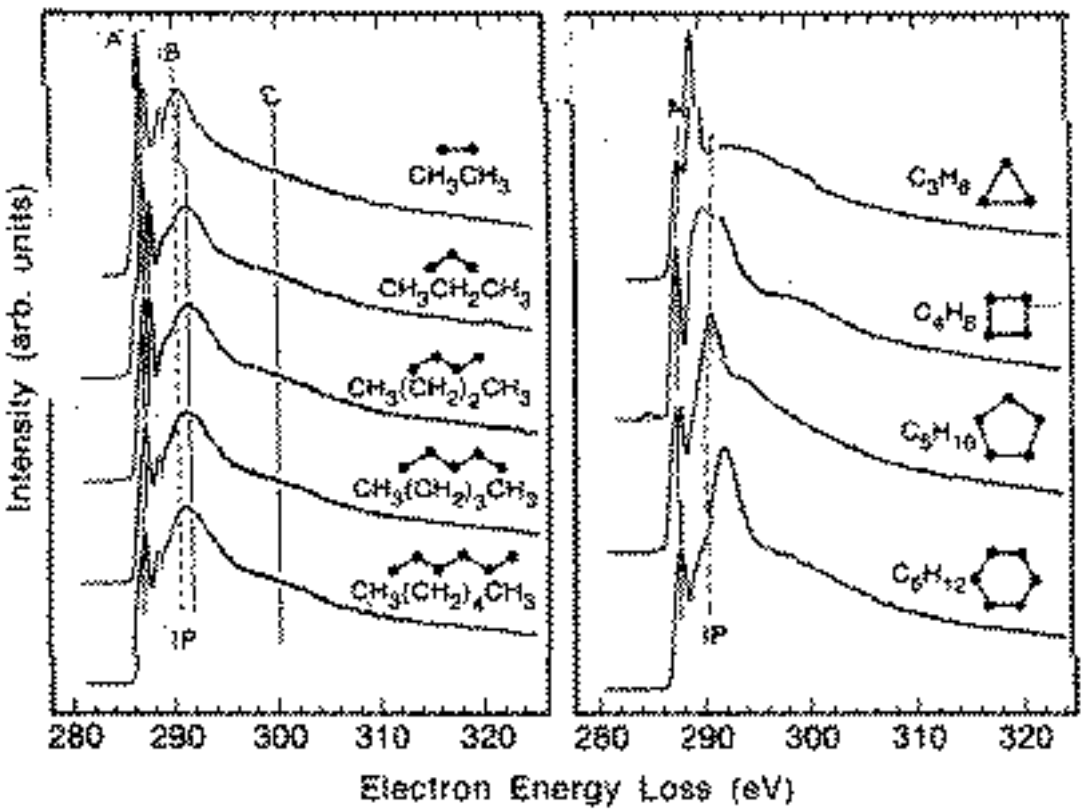
X-ray Absorption (NEXAFS)



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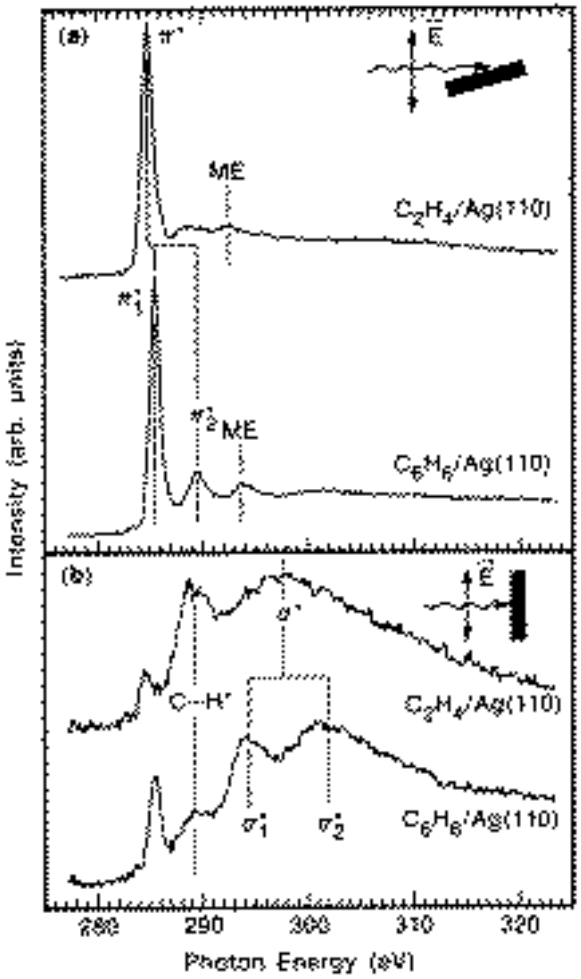
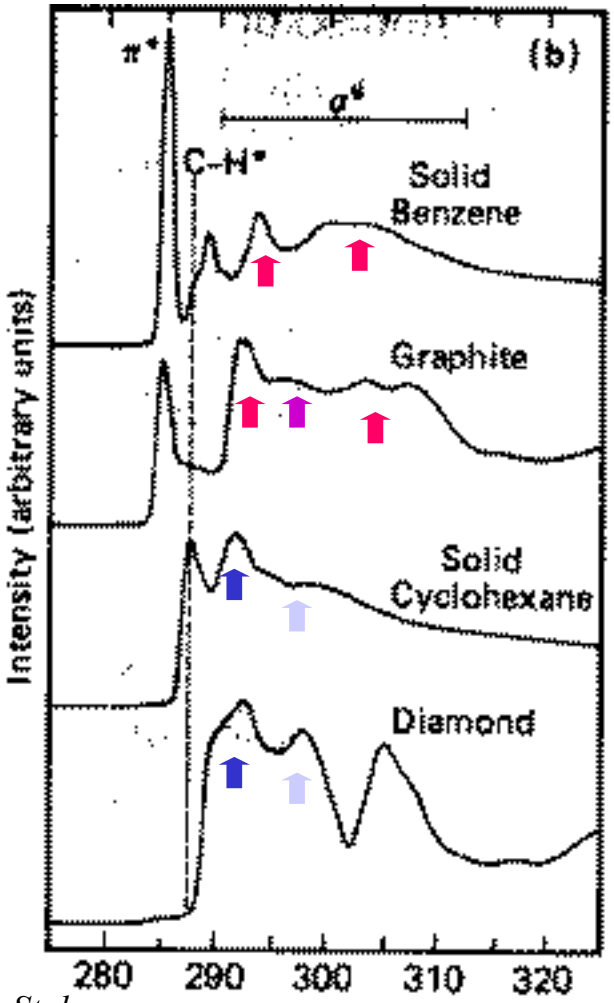


σ bond interaction between alifatic molecules is weak

σ bond interaction between aromatic molecules is stronger

X-ray Absorption (NEXAFS)



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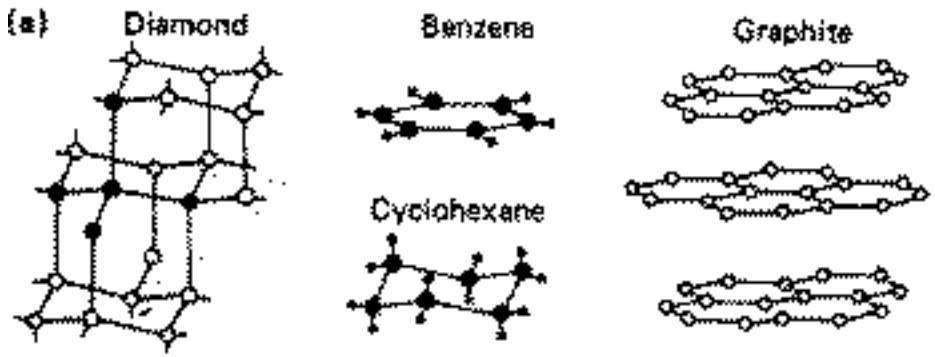
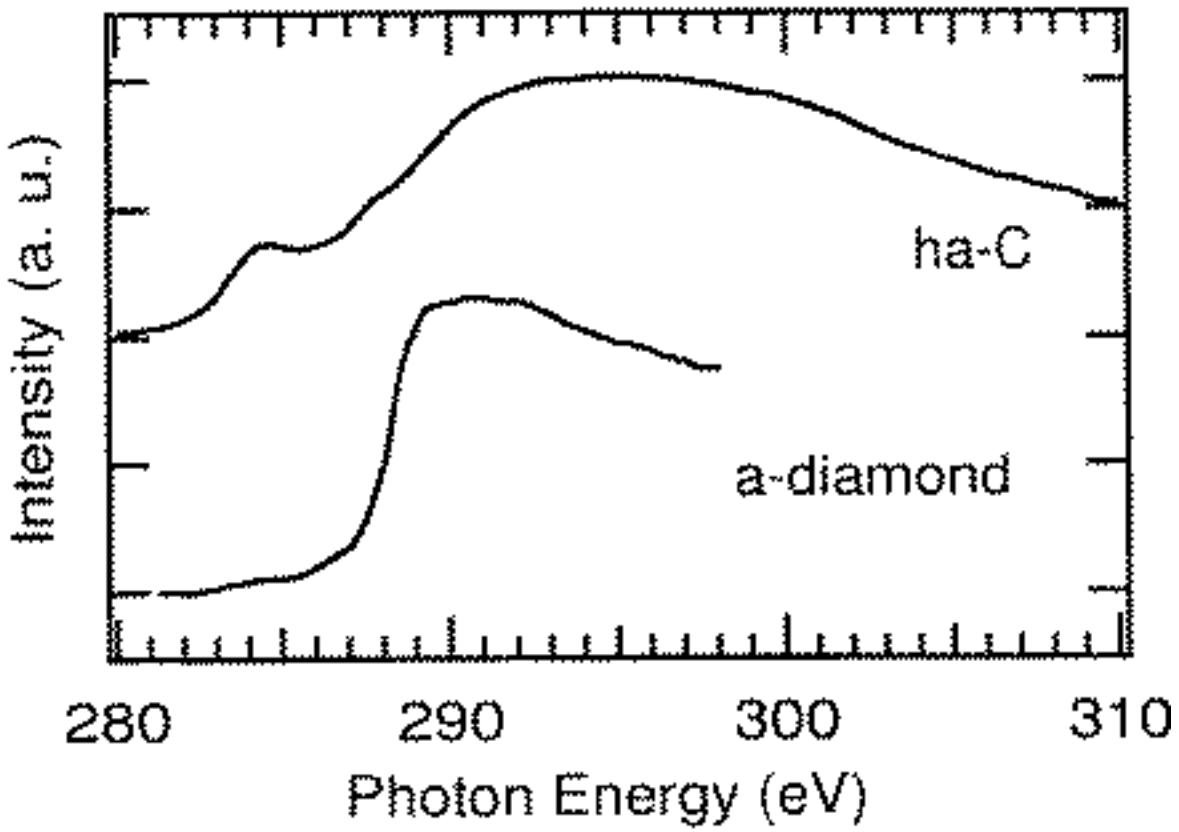


- ***"Building block" picture: from molecules to crystals***

X-ray Absorption (NEXAFS)

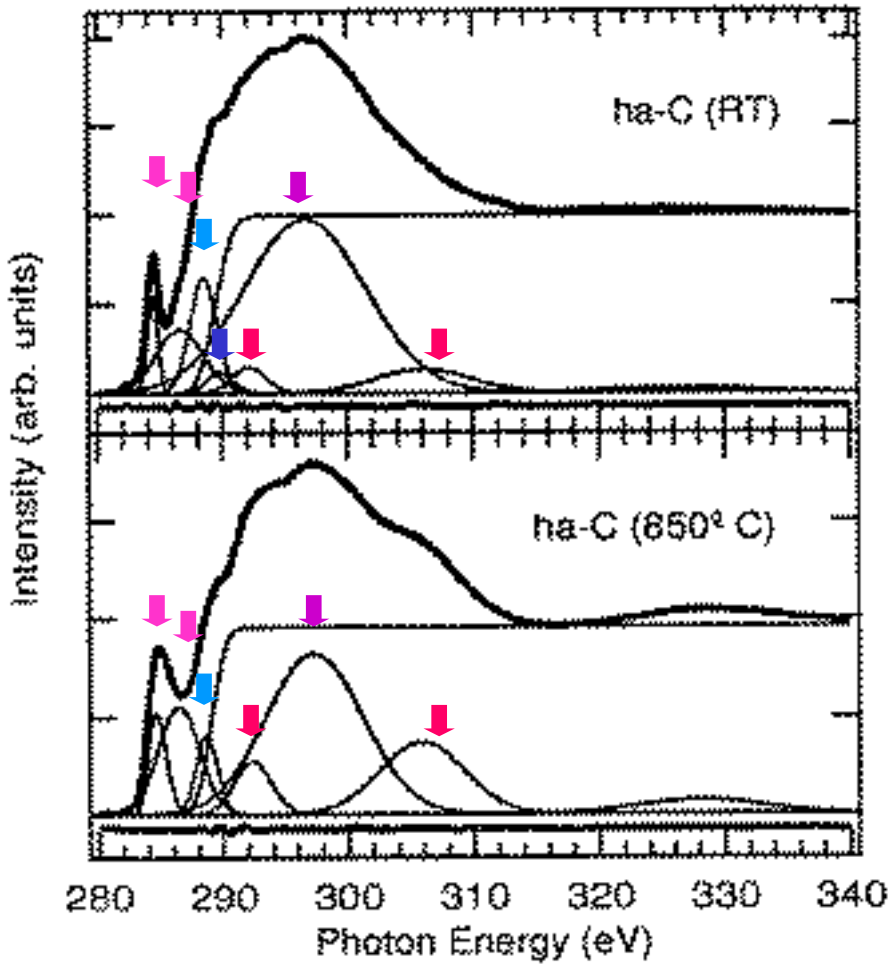


H. Hirai et al.
Phys. Rev. B ***60*** *(1999), 6357*

• σ^* *from* sp^3 *atoms are in the region 288-292 eV*

X-ray Absorption (NEXAFS)

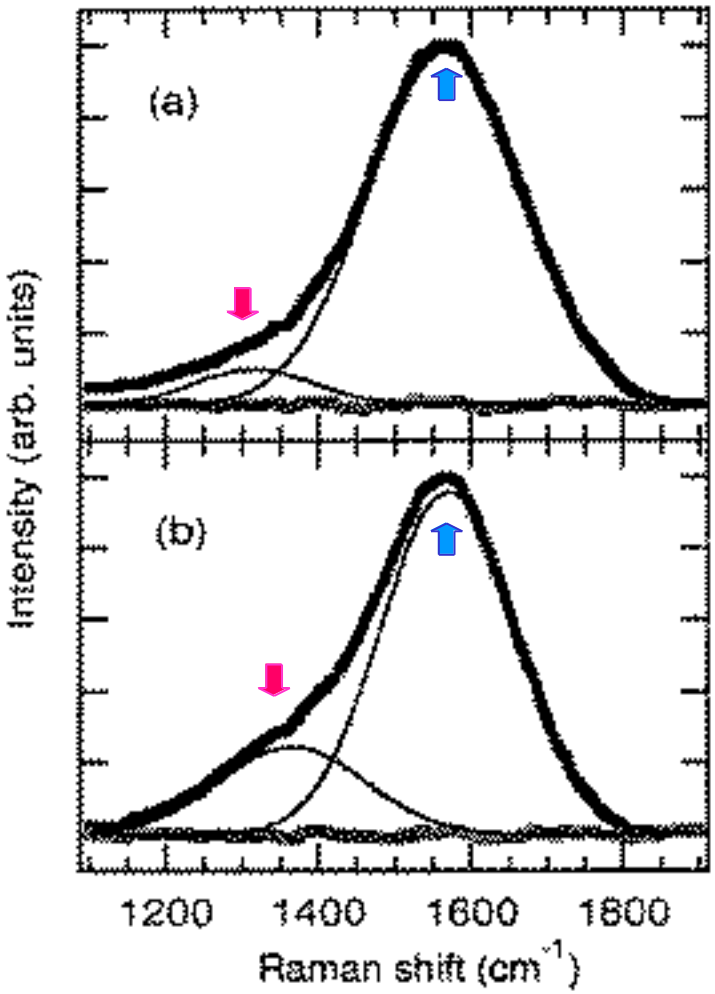
Components:

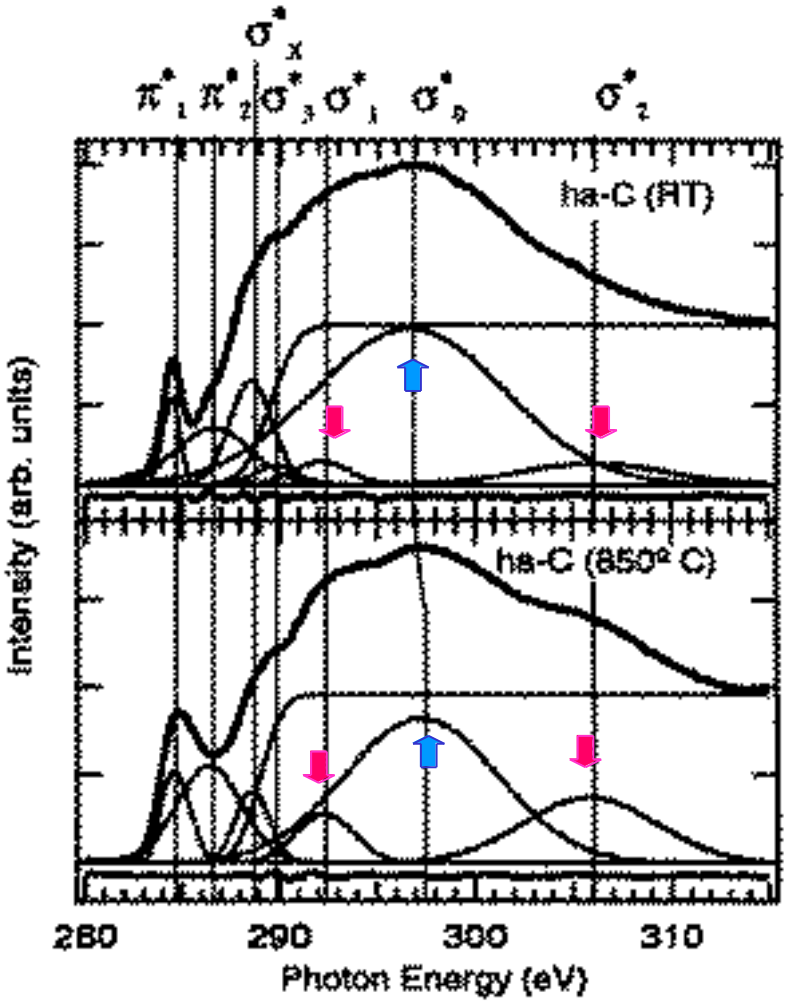


- *"non-conjugated" sp^2*
- *conjugated sp^2*
- *sp^3 bonded*
- *π^* band*

X-ray Absorption (NEXAFS)

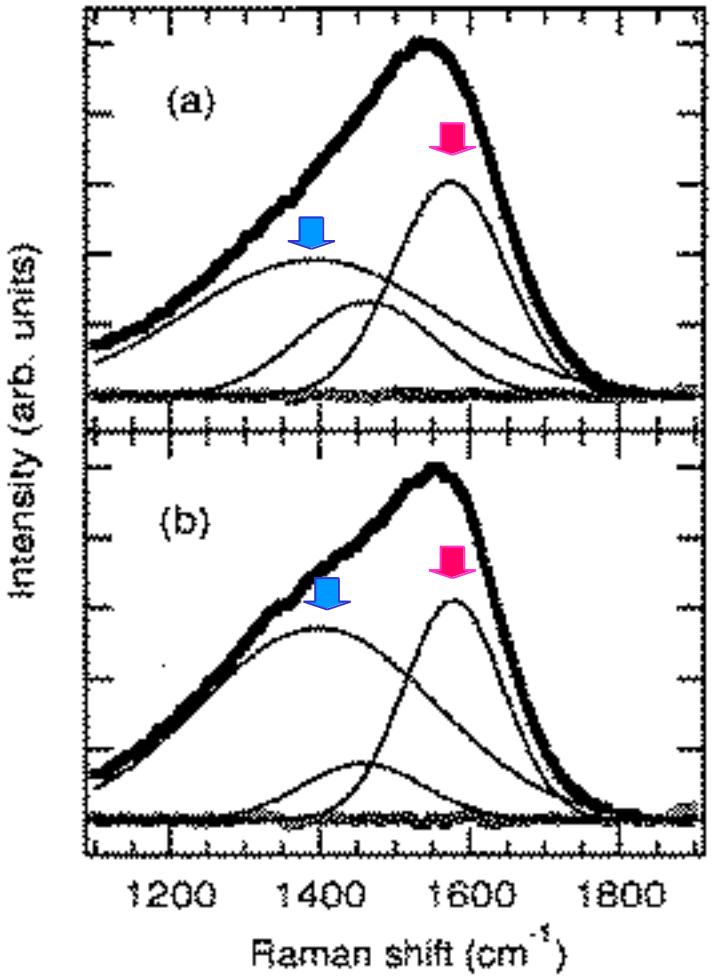
*Correlation Raman - NEXAFS in **hard a-C***

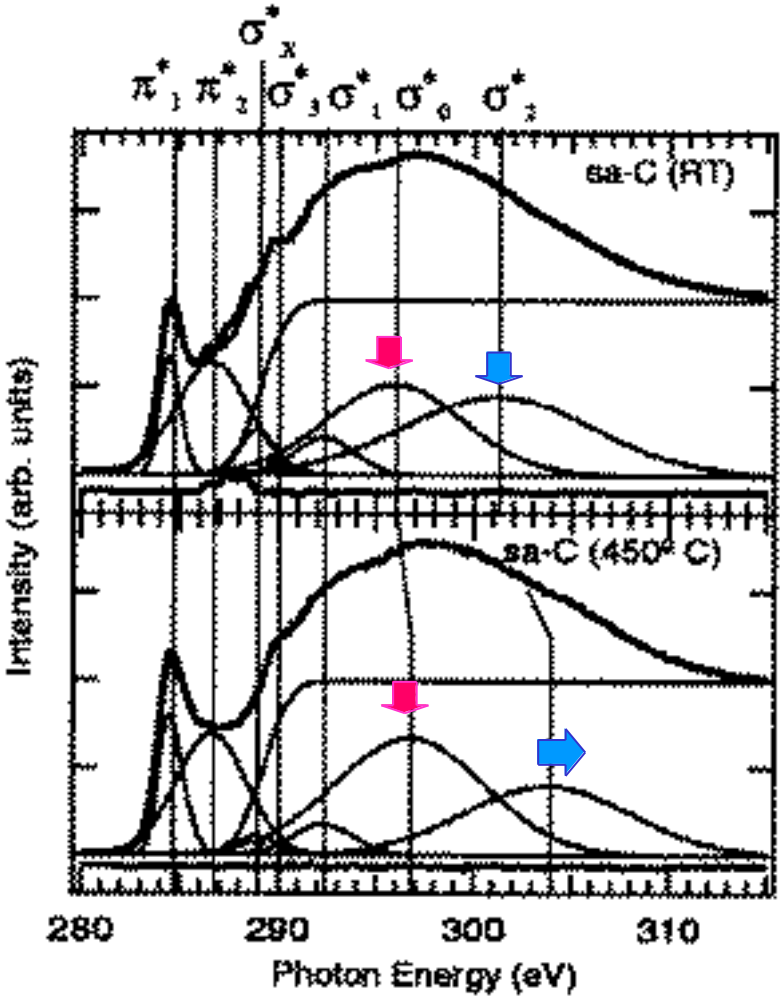




X-ray Absorption (NEXAFS)

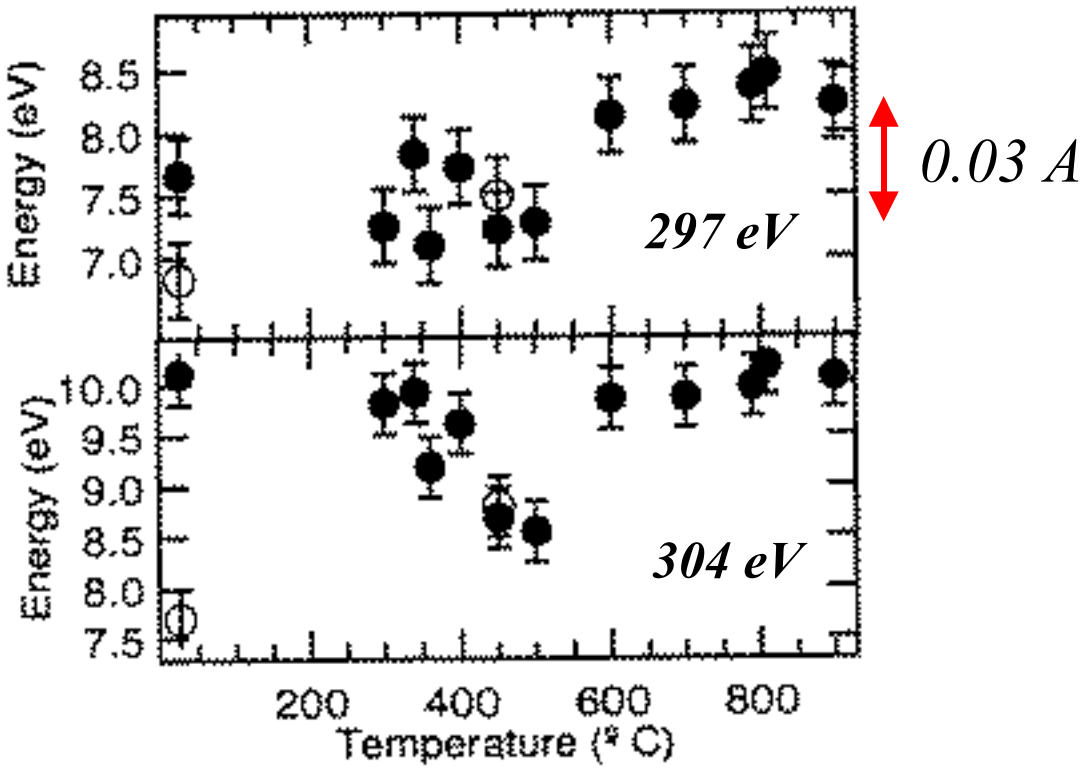
Correlation Raman - NEXAFS in soft a-C





X-ray Absorption (NEXAFS)

σ^* energy with respect to E_{vac}



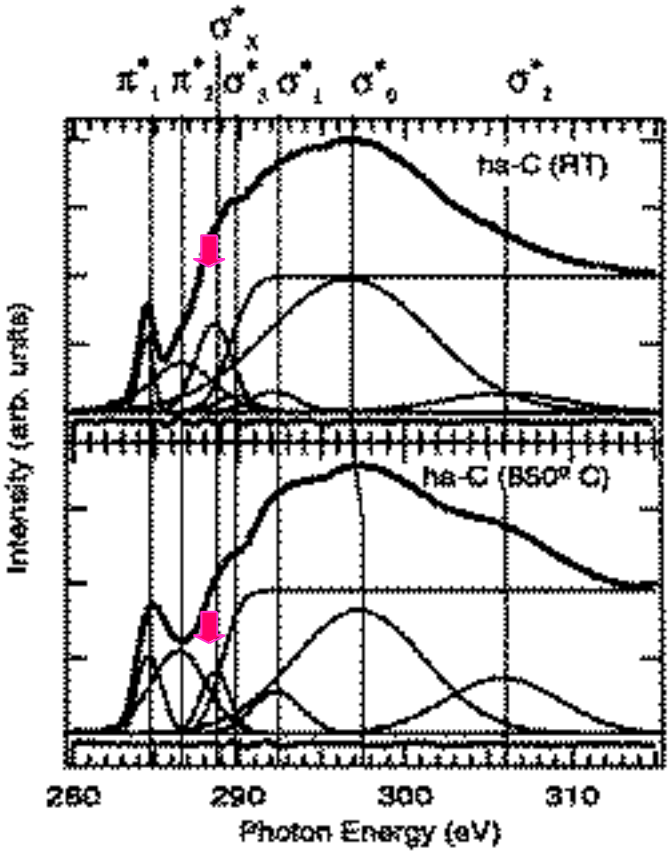
"Phase transition" between 450° C and 600° C (detected through σ^* binding energy):

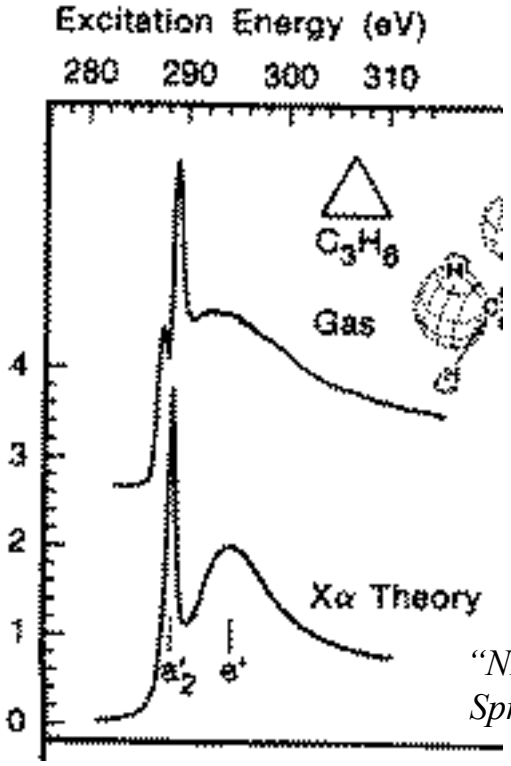
sp^2 bond length shrinks

X-ray Absorption (NEXAFS)

*Component at **288.5 eV**:*

- ***Decreases with T***
- ***Lower in "soft" sa-C***





J. Stohr
"NEXAFS Spectroscopy"
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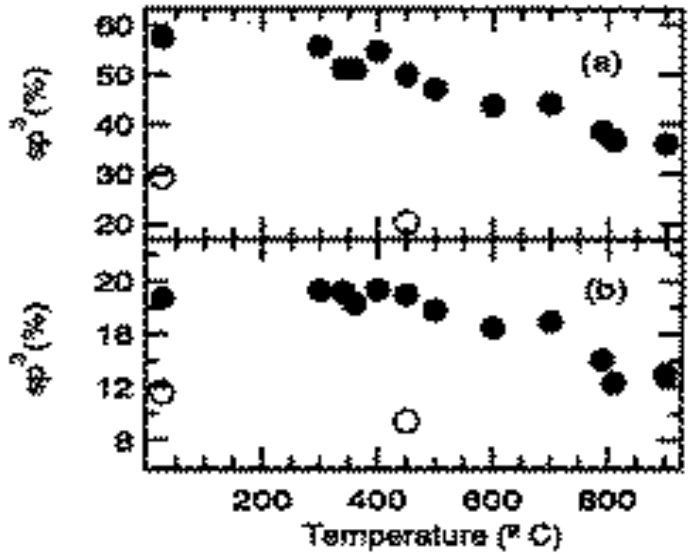
***Cyclopropane**: strained σ bond (bond angle ~ 60°!)*

X-ray Absorption (NEXAFS)

Analysis allows:

- ***Separation of π* from σ* states***
- ***Assignment of σ* component to the type of bonding***

sp^3 estimation in two different ways



←π*/σ*

←σ^*_{sp3}/σ^*

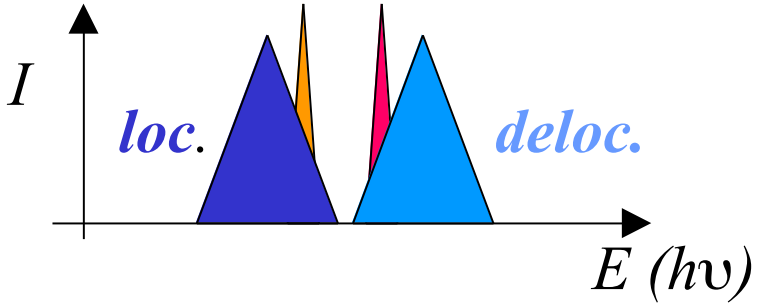
X-ray Absorption (NEXAFS)

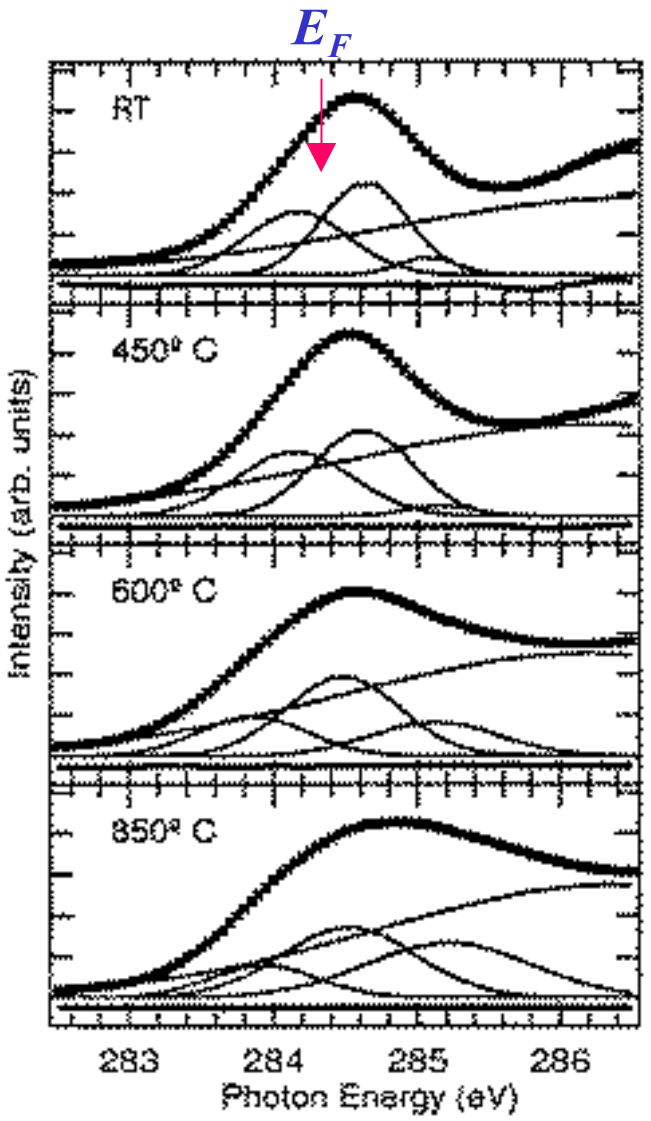
Sructure in π*

•*Correlation XPS & NEXAFS:*

$$XPS \longrightarrow Solid^{+}$$

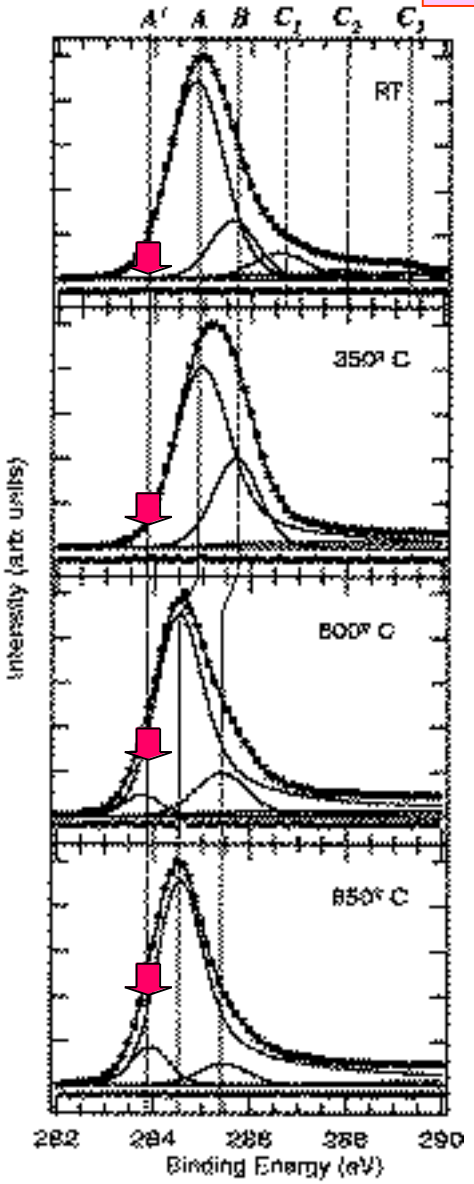
$$NEXAFS \longrightarrow (Solid^{+})^{-}$$

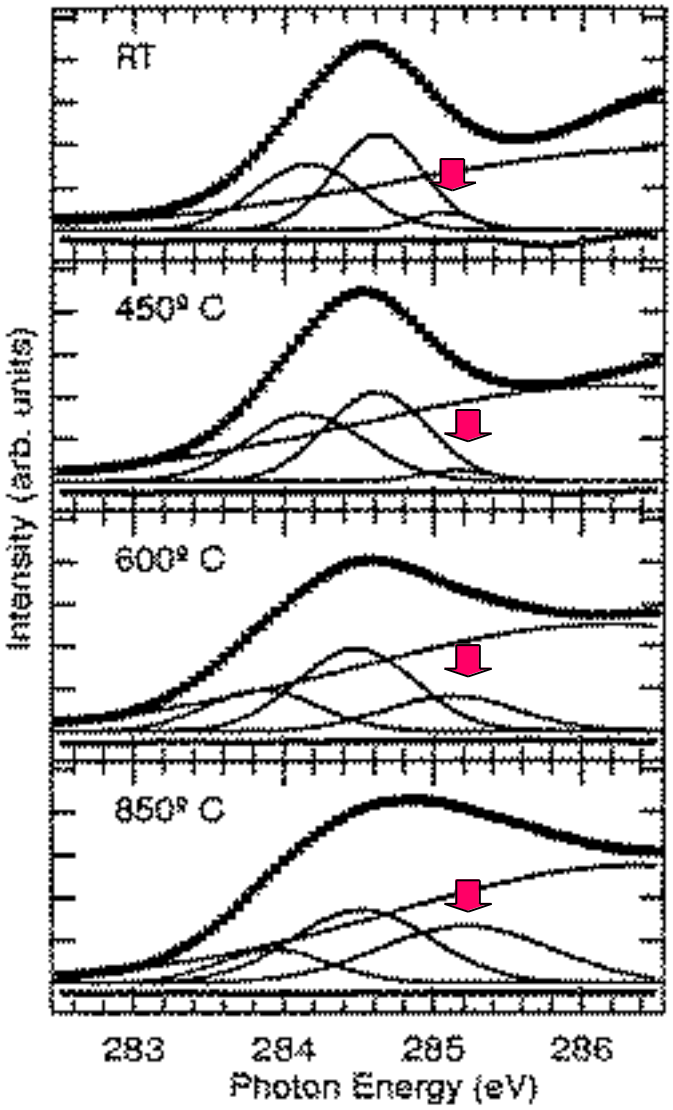




X-ray Absorption (NEXAFS)

Correlation XPS & NEXAFS @ π?*





CONCLUSIONS

Analisis of NEXAFS spectra of a-C as a BIG POLYMER:

- ***Consistent with Raman and photoemission spectroscopies***

- ***Allows separación of π^* states from σ^* states:***
  - ***+ Bond selective technique: changes in bond length for each type of bond.***
  - ***+ sp^3 bonding as cyclopropane***
  - ***+ different, and more fundamental way of sp^3/sp^2 estimation***

- ***Sharp structural and electronic changes at ~ 550ºC***